

SPECIFICATION

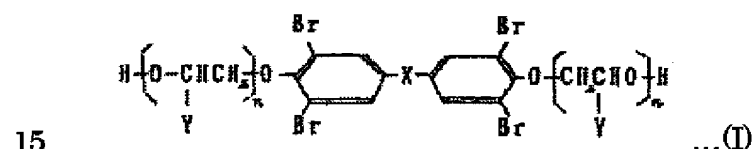
1. TITLE OF INVENTION

FLAME RETARDENT POLYESTER FIBER AND METHOD OF PRODUCING THE SAME

2. CLAIMS

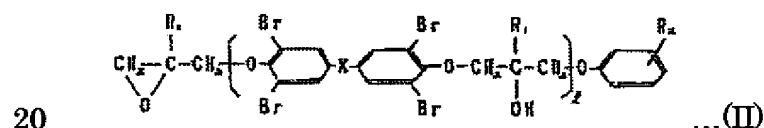
- 1) A flame retardant polyester fiber containing:
relative to 100 parts by weight of polyester composed principally of polyethylene terephthalate,

0.1 to 8 parts by weight of at least one kind of a halogenated diol compound represented by the formula (I),



(where X is a methylene group, an isopropylidene group or a sulfonyl group, Y is H or a methyl group and n is an integer of 1 to 3), and

0.1 to 8 parts by weight of a halogenated glycidyl ether compound represented by the formula (II),



(where R₁ is H and/or a CH₃ group, R₂ is H or an alkyl group of C₁ to C₄, X is a methylene group, an isopropylidene group or a sulfonyl group, and l is an integer of 1 or more),

wherein a total amount of the halogenated diol compound and the halogenated glycidyl ether compound is 0.3 to 10 parts by weight.

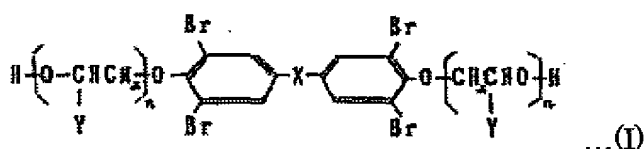
- 2) The fiber according to claim 1, wherein at least 85 weight % of the polyester is polyethylene terephthalate.

3) The fiber according to claim 1, wherein X in the halogenated diol compound and the halogenated glycidyl ether compound is an isopropylidene group.

5 4) The fiber according to claim 1, wherein the total amount of the halogenated diol compound and the halogenated glycidyl ether compound is 0.5 to 8 parts by weight.

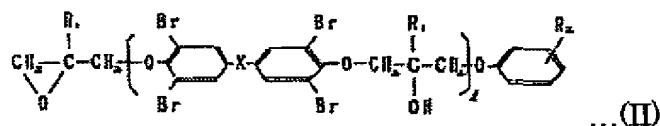
5) A method of producing a flame retardant polyester fiber, comprising:
10 when melt-spinning polyester composed principally of polyethylene terephthalate,

mixing, with 100 parts by weight of the polyester, 0.1 to 8 parts by weight of at least one kind of a halogenated diol compound represented by the formula (I),



15 (where X is a methylene group, an isopropylidene group or a sulfonyl group, Y is H or a methyl group and n is an integer of 1 to 3) and

0.1 to 8 parts by weight of a halogenated glycidyl ether compound represented by the formula (II),



20 (where R₁ is H and/or a CH₃ group, R₂ is H or an alkyl group of C₁ to C₄, X is a methylene group, an isopropylidene group or a sulfonyl group, and l is an integer of 1 or more),

wherein a total amount of the halogenated diol compound and the halogenated glycidyl ether compound that are mixed with the polymer is 0.3 to 10
25 parts by weight.

6) The method according to claim 5, wherein at least 85 weight % of the polyester is polyethylene terephthalate.

7) The method according to claim 5, wherein X in the halogenated diol compound and the halogenated glycidyl ether compound is an isopropylidene group.

5 8) The method according to claim 5, wherein the total amount of the halogenated diol compound and the halogenated glycidyl ether compound is 0.5 to 8 parts by weight.

9) The method according to claim 5, wherein the mixing is carried out by rapid
10 kneading with the use of a static kneading element.

3. DETAILED DESCRIPTION OF INVENTION

(Field of industrial application)

The present invention relates to a flame retardant polyester fiber and a
15 method of producing the same, and more particularly to a polyester fiber having anti-pill and flame retardant characteristics and a method of producing the same.

(Prior art)

Industrially, polyester has been used widely in fibers, films and plastics. It, however, has a weak point of being vulnerable to combustion. With the recent moves
20 afoot to tightening laws and regulations on fire prevention, flame retardant polyester has been strongly demanded.

Conventionally, a variety of studies have been conducted on making polyester flame retardant. However, a method that offers an excellent balance of a flame retardant performance, production conditions and general quality has not been
25 established yet.

As a method of making polyester durably flame retardant, a halogenated compound, a phosphorous compound and a phosphorus-containing halogenated compound are copolymerized with or added to and mixed with the polyester.

JP S49-54494 A discloses a method of copolymerizing a halogenated
30 compound with polyester. As a method of adding a phosphorous compound and the like to the obtained copolymer in order to improve the thermal stability of the copolymer, improvement techniques described in JP S50-82160 A, JP S50-78646 A,

JP S50-67354 A, JP S50-34395 A and the like have been known.

Further, as an adding/mixing method, as described in JP S52-24943 A, it has been known to mix a halogen-containing phosphorous compound with polyester.

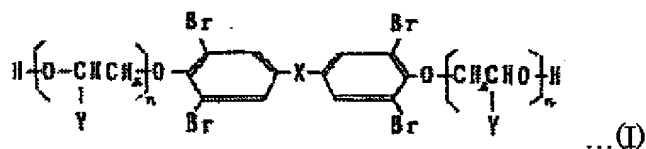
(Problem to be solved by the invention)

5 When a halogenated compound is copolymerized with polyester to make the polyester flame retardant, the thermal stability of the obtained flame retardant polyester significantly drops, causing coloring and troubles related to the production due to the heat at the time of molding. Further, with the adding/mixing method, since the compounds are merely kneaded with polyester, falling is caused by a solvent
10 treatment such as dry cleaning. Thus, there is a drawback to the duration of the effect with this method. As a result of eagerly studying a simple and easy method of producing flame retardant polyester that does not cause troubles such as thermal cracking during the production and a way to improve the duration of effects of the flame retardant polyester that is produced by the method, the inventors have perfected
15 the present invention.

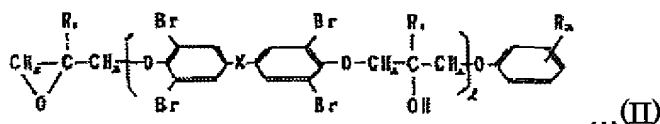
 An object of the present invention is to provide durable flame retardant polyester. Another object of the present invention is to provide a method of producing the polyester industrially and uniformly at low cost and with ease. Yet another object of the present invention is to provide flame retardant polyester as a fiber having
20 anti-pill and flame retardant characteristics, which can be use for clothing purposes.

(Means for solving problem)

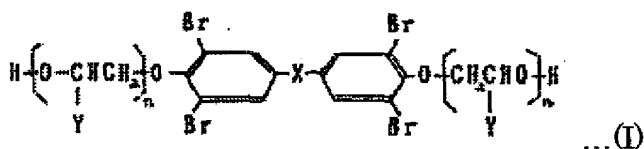
 That is, the present invention provides a flame retardant fiber that contains, relative to 100 parts by weight of polyester composed principally of polyethylene
25 terephthalate, 0.1 to 8 parts by weight of at least one kind of a halogenated diol compound represented by the formula (I),



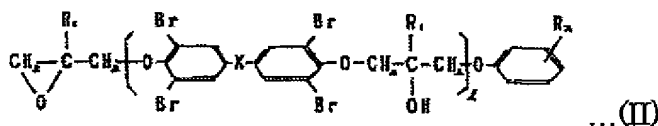
(where X is a methylene group, an isopropylidene group or a sulfonyl group, Y is H or a methyl group and n is an integer of 1 to 3), and 0.1 to 8 parts by weight of a
30 halogenated glycidyl ether compound represented by the formula (II),



(where R₁ is H and/or a CH₃ group, R₂ is H or an alkyl group of C₁ to C₄, X is a methylene group, an isopropylidene group or a sulfonyl group, and l is an integer of 1 or more). A total amount of the halogenated diol compound and the halogenated glycidyl ether compound that are contained in the fiber is 0.3 to 10 parts by weight. The method of the present invention comprises, when melt-spinning polyester composed principally of polyethylene terephthalate, mixing, with 100 parts by weight of the polyester, 0.1 to 8 parts by weight of at least one kind of a halogenated diol compound represented by the formula (I),



(where X is a methylene group, an isopropylidene group or a sulfonyl group, Y is H or a methyl group and n is an integer of 1 to 3) and 0.1 to 8 parts by weight of a halogenated glycidyl ether compound represented by the formula (II),



(where R₁ is H and/or a CH₃ group, R₂ is H or an alkyl group of C₁ to C₄, X is a methylene group, an isopropylidene group or a sulfonyl group, and l is an integer of 1 or more). A total amount of the halogenated diol compound and the halogenated glycidyl ether compound that are mixed with polyethylene terephthalate is 0.3 to 10 parts by weight.

Polyalkylene terephthalate that is applied to the present invention is preferably composed at least of 85 weight % of polyalkylene terephthalate. As dicarboxylic acid other than terephthalic acid, one or two or more kinds of aromatic carboxylic acids such as isophthalic acid, naphthalene dicarboxylic acid, trimellitic acid and 5-sodium sulfoisophthalic acid, aliphatic dicarboxylic acids such as adipic acid, sebacic acid and glutaric acid, and glycols other than ethylene glycol and butylene glycol such as diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol,

polypropylene glycol, tetramethylene glycol, pentamethylene glycol, neopentyl glycol, hexamethylene glycol may be copolymerized with each other. However, polyethylene terephthalate is particularly preferable.

It is preferable that the polyester that is applied to the present invention has
5 an average molecular weight of 18,000 to 22,000.

The halogenated diol compound that is applied to the present invention is represented by the above-mentioned formula (I). Although X can be any of a methylene group, an isopropylidene group and a sulfonyl group, an isopropylidene group is preferable. Further, in order to improve the thermal resistivity of the
10 compound, it is possible to use a mixed compound of the halogenated diol compound with an isopropylidene group and that with a sulfonyl group. Further, although Y in the formula is H or a methyl group, H is preferable in terms of the thermal resistivity. In terms of the reaction with the polyester, it is particularly preferable that n is 1. Furthermore, it is preferable that the hydroxyl value of the halogen-containing
15 compound is 200 or less.

The halogenated glycidyl ether compound, which is mixed with the polyester together with the halogenated diol compound, is represented by the above-mentioned formula (II). H and/or a methyl group is applied to R₁. In particular, H is preferable in terms of the thermal resistivity and generality. Although H or an alkyl group of C₁
20 to C₄ is applied to R₂, a methyl group, an ethyl group, a propyl group or a butyl group is preferable and an isobutyl group is particularly preferable in terms of the thermal resistivity and generality as similarly to R₁. Although X can be any of a methylene group, an isopropylidene group and a sulfonyl group, an isopropylidene group is preferable. Further, in order to improve the thermal resistivity of the compound, it is
25 possible to use a mixed compound of the halogenated glycidyl ether compound with an isopropylidene group and that with a sulfonyl group. Moreover, although an integer of 1 or more is applied to l, an integer of 1 to 8 is preferable and an integer of 1 to 6 is particularly preferable.

Specifically, the halogenated glycidyl ether compound is produced by
30 ring-opening diglycidyl ether of at least one kind of a halogen-containing aromatic bis-hydroxy derivative with the use of at least one kind of a monofunctional compound. Examples of the aromatic bis-hydroxy derivative include halogen compounds such as

bisphenol A, bisphenol F, bisphenol S, bromized bisphenols, bisphenols added with ethylene oxide and/or propylene oxide, bis-(β -hydroxyethyl) terephthalate and bis-(β -hydroxyethyl) isophthalate.

Further, examples of the monofunctional compound include alcohols such as
5 methyl alcohol, ethyl alcohol, amino alcohol and benzyl alcohol and alkylphenols such as phenol, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2,3-dimethylphenol, 2,4-dimethylphenol, 2,6-dimethylphenol, 3,4-dimethylphenol, 3,5-dimethylphenol, 2-ethylphenol, 3-ethylphenol, 4-ethylphenol, 2-propylphenol, 3-propylphenol, 4-propylphenol, 2-tert-butyl phenol, 3-tert-butyl phenol, 4-tert-butyl phenol,
10 2-sec-butyl phenol, 4-sec-butyl phenol, 2-n-butyl phenol, 3-n-butyl phenol, 4-n-butyl phenol, 4-methyl-2-tert-butyl phenol, 4-tert-aminophenol, 6-n-amyl phenol, 4-methyl-2-tert-amyl phenol, 2,5-dimethyl-4-tert-butyl phenol, 4-ethyl-2-tert-butyl phenol, 2,6-di-tert-butyl phenol, 4-diisobutyl phenol, 3-methyl-4,6-di-tert-butyl phenol, 3-methyl-4diisobutyl phenol,
15 2,3-dimethyl-4,6-di-tert-phenol, 3-ethyl-4,6-di-tert-butyl phenol, 4-methyl-2,6-di-tert-amyl phenol and 2,4,6-tri-tert-butyl phenol. In particular, tert-butyl phenol, sec-butyl phenol or a-butyl phenol is preferable. Other examples of the monofunctional compound include phenyl glycidyl ether, metacresol glycidyl ether and tert-butylphenol glycidyl ether.

20 With 100 parts by weight of the polyester, 0.1 to 8 parts by weight, preferably 0.2 to 6 parts by weight and particularly 0.5 to 5 parts by weight of the halogenated compounds is mixed. With 100 parts by weight of the polyester, 0.1 to 8 parts by weight, preferably 0.2 to 6 parts by weight and particularly 0.5 to 5 parts by weight of the halogenated glycidyl ether is mixed. Relative to 100 parts by weight of the
25 polyester, the total amount of the halogenated diol compound and the halogenated glycidyl ether compound is 0.3 to 10 parts by weight, preferably 0.5 to 8 parts by weight and particularly 1 to 5 parts by weight.

When the total amount of the halogenated diol compound and the halogenated glycidyl ether compound is smaller than the above-mentioned ranges, the
30 effect of the flame retardant characteristic may be insufficient in some cases. In contrast, when the total amount is larger than the above-mentioned ranges, troubles related to the production, such as single yarn breakage at the time of spinning, are

likely to occur.

A dye, pigment, fluorescent brightening agent, flatting agent, brightener, foaming agent, antistatic agent, thermal and light stabilizers, all of which are commercially available, can be added to the compounds that are applied to the present invention.

As a method of adding the halogenated diol compound and the halogenated glycidyl ether compound to the polyester of the present invention, it is possible to mix the compounds with the polyester by using a static mixer at the time of chipping or to stir and mix the compounds with the polyester in a chipped state. However, to enjoy efficiencies of scale of the production such as continuation, it is preferable that the compounds are added to the polyester at the time of spinning. Although chip spinning can be employed as spinning, direct spinning is desired in terms of uniformity in the quality. To add the compounds to the polyester at the time of spinning, for example, a gathering portion is formed in the outlet of a polymer introduction tube, and the halogenated diol compound and the halogenated glycidyl ether compound that are measured with a plunger pump or gear pump are injected, in a mixed state, into the polyester having a normal degree of polymerization.

Subsequent to the gathering portion, a polymer channel is composed in order of a first kneading portion, a gear pump, a second kneading portion, a spin beam (third kneading portion) and a spinning pack. By increasing an allowable pressure loss in each of the kneading portions as much as possible, it is possible to increase the number of known static kneading elements that are used. Examples of the static kneading elements include a static mixer (manufactured by Kenics Corp.), ROSS-LSG mixer (manufactured by Tokush Kika Kogyo Inc.), SM mixer (manufactured by Sulzer Ltd.) and BKM mixer (manufactured by Sulzer Ltd.). By incorporating the gathering portion, the first kneading portion and the gear pump in a wear plate for jointing the gear pump, it is possible to increase the accuracy in measuring additives and to make the device compact.

Although it is possible to obtain a fiber having excellent flame retardant and anti-pill characteristics by using the halogenated diol compound alone, this involves troubles related to the production. In other words, since the viscosity or molten viscosity is small and the measuring and discharging of the additives become

insufficient, the addition becomes uneven and the mixing and dispersion become insufficient. As a result, single yarn breakage occurs frequently at the time of spinning, which often involves machine stoppage due to single yarn wounding at the time of drawing.

5 Since the halogenated diol compound and the halogenated glycidyl ether compound of the present invention have sufficient thermal resistivity and stable viscosity and can uniformly be discharged, it is possible to produce a polyester fiber having flame retardant and anti-pill characteristics in a stable manner.

10 (Effects of the invention)

The flame retardant polyester fiber obtained by the present invention has an excellent anti-pill characteristic. Thus, it is not only used widely for clothing purposes but also is preferably used in the areas of wadding and non-woven fabric.

15 (Examples)

Hereinafter, Examples of the present invention will be described.

The flame retardant performance was in conformity with "Standards for Performance Test of Flame Repellent Products" (beddings), a second appendix to No. 69 of Shoboyo (April 1, 1982), and was evaluated on the basis of the carbonized length
20 (mm) under the 45° methenamine basket method and the number of times of flame contact under the 45° coil method. Further, the anti-pill characteristic was measured using an ICI pilling tester (5 Hrs) in a state where the fabric was tubular knitted.

Example 1

25 The gathering portion was formed in the outlet of the polymer introduction tube, and an adduct having 2 moles of EO units added to tetrabromobisphenol A and a halogenated glycidyl ether compound (epoxy equivalent: 2800, melting point: 105°C, Br cont: 47.8%) obtained by ring-opening tetrabromobisphenol A glycidyl ether with the use of p-sec butylphenol were metered using the gear pump in a mixed state at a
30 certain ratio, and 2.0 weight % of the mixture was added to polyethylene terephthalate heated to 280°C and having an average molecular weight of 20,000. Note that the halogenated diol compound had a melting point of 118 °C and the hydroxyl value was

178.

To measure the rapid reaction of the compound, a static mixer (manufactured by Kenics Corp.) 12 element having a L/D ratio of 1.5 and a BKM mixer (manufactured by Sulzer Ltd.) 2 element were used in the polymer channel, and further a BKM mixer 5 element was used in the spin beam. A spinneret was attached to the spinning pack, and a fully oriented yarn of a single yarn of 2 deniers was obtained through a normal spin and drawn process.

After the fully oriented yarn had been cut to 51 mm, spun by ring spinning to be 20'S, and tubular knitted, the number of times of flame contact under the 45° coil method and the anti-pill characteristic using an ICI pilling tester (5 Hrs) were measured. Table 1 provides the results. Note that the flame retardant characteristic was tested after the tubular knitted fabric had been washed for five times.

[TABLE 1]

Contents (weight %)		Number of times of flame contact (times)	Anti-pill characteristic (grade)	Spinning condition
Halogenated diol compound	Halogenated glycidyl ether compound			
2.0	0	4	4 to 5	poor
1.8	0.2	4	4 to 5	somewhat poor
1.6	0.4	4	4	good
1.2	0.8	4	3 to 4	as above
0.8	1.2	3	4	as above
0.4	1.6	3	3	as above
0.2	1.8	3	3	as above
0	2.0	3	2	as above

15

Example 2

Similarly to Example 1, the ratio between the halogenated diol compound and the halogenated glycidyl ether compound was changed to 6 to 4, and the content relative to the polyester was changed in a range of 0 to 12 weight %, and fully oriented yarns of 3 deniers were obtained from the respective fibers. After each yarn had been cut to 51 mm, spun by ring spinning to be 20'S with 100% of polyester, and tubular knitted, the number of times of flame contact under the 45° coil method and the anti-pill characteristic using an ICI pilling tester (5 Hrs) were measured. Table 2 provides the results. Note that the flame retardant characteristic was tested after

each tubular knitted fiber had been washed for five times.

[TABLE 2]

Contents (weight %)	Number of times of flame contact (times)	Anti-pill characteristic (grade)	Condition of spin and drawn operation
0	1.6	1	good
0.3	1.9	2	as above
0.5	2.5	3	as above
2	4	3 to 4	as above
3	4.5	4	as above
5	5	4 to 5	as above
8	as above	5	as above
10	as above	as above	some what poor
12	as above	as above	poor

Example 3

5 Polyethylene terephthalate having an average molecular weight of 21,000, which was polymerized using direct continuous polymerization, was molten at a polymer tube temperature of 282 °C, and 50 parts by weight of an EO adduct of a mixture (weight ratio = 1:1) of tetrabisphe-
 10 nol A and tetrabisphe-
 nol S and 50 parts by weight of a halogenated glycidyl ether compound (epoxy equivalent: 3870, softening point: 138 °C, Br cont: 53.6%) obtained by ring-opening tetrabromobisphenol A glycidyl ether with the use of t-butylphenol glycidyl ether were molten, mixed with each other and metered using the gear pump. 1.5 weight % of the mixture was added to the polyester. Note that these halogenated diol compounds had a melting point of 145 °C and 93% of the EO adduct was an adduct having 2 moles of EO units.

15 Similarly to Example 1, a static mixer was used to measure the rapid reaction.

A pack having a hollow-body nozzle was inserted in the spin beam, and a non-oriented yarn of a single yarn of 23.6 deniers was spun at a discharge rate of 900 g/min and spinning speed of 765 m/min. The non-oriented yarn was drawn by 4.5 times, crimping of 10 times/inch was added to the yarn using a crimper, and polyester
 20 cotton of 6d × 51 mm was obtained.

Futon wadding was produced from the cotton and the flame retardant characteristic was tested on the basis of the methenamine 45° basket method. Favorable results were obtained as the maximum carbonized length was 95 mm and the average carbonized length was 84 mm.